DESIGN SPECIFICATIONS FOR A POROUS COMPOSITE LSM/YSZ CATHODE FOR SOLID OXIDE FUEL CELLS

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Abstract

In this paper, the optimal microstructure and thickness of a LSM/YSZ composite cathode for a solid oxide fuel cell was specified using a physically-based, fully transient continuum model. The model captured the intricate and complex coupling of porous media transport phenomena to heterogeneous and electro-chemistry using first principle conservation equations of mass, species and charge. Oxygen reduction kinetics were modeled using a detailed mechanism of elementary reactions without the assumption of rate limiting step(s). A parametric study revealed the set of design parameters, e.g. YSZ volume fraction, particle size and cathode thickness that minimized the overall polarization resistance. The simulated results were found to be in good agreement with literature data.

Keywords

Solid oxide fuel cells, LSM/YSZ composite electrode, modeling, electrochemical impedance, electrode microstructure, electrode design

Introduction

The electrochemical performance of a solid oxide fuel cell has long been plagued by the slow kinetics of oxygen reduction at the cathode, causing it to be the most dominant source of polarization losses in the cell (Tu and Stimming (2004)). Through the addition of an ion-conducting phase to the existing electron-conducting phase, porous composite cathodes attempt to alleviate the problem by increasing the electrochemically active region. One of the earliest and most widely used composites is $La_{1-x}Sr_xMnO$ co-sintered with 8% Y_2O_3 doped ZrO_2 due to its mechanical and chemical stability (Adler (2004)).

Prior experimental and modeling work have tried to elucidate the mechanism for oxygen reduction at the LSM/YSZ interface but a consensus has not yet been reached on the rate-limiting step since it is dependent on the cathode microstructure. Physically based models are especially useful in these circumstances since they are capable of analyzing the interaction between microstructure and kinetics in great detail with Chen et al. (2004) and Pakalapati et al. (2014) having demonstrated the utility of such models specifically for LSM-YSZ composite cathodes.

In this study, a fully transient continuum half-cell model is developed based on the approach developed by Bessler et al. (2007) and Goodwin et al. (2009) to ascertain the optimal design specifications of a LSM/YSZ composite cathode.

Approach

The continuum half-cell model assumes mass, species and charge transport to be one-dimensional through the thickness of the cathode. The complete reaction diffusion equation is solved to obtain gas phase species mass

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fractions and total fluid density whereas the solution of the distributed charge transfer model provides electronic and ionic phase potentials at every node. Gas phase species fluxes which serve as input to the reaction diffusion equation are evaluated using the Dusty-Gas model.

The transport equations are coupled to reaction source terms which are described using an Arrhenius ansatz. The model employs a spillover-based detailed reaction mechanism previously developed by the authors (Banerjee and Deutschmann (2015)) and does not assume any rate limiting steps. All effective transport parameters required by the model are evaluated using percolation theory. On application of the appropriate boundary conditions, the model computes steady-state current densities for an applied potential difference. Electrochemical impedance spectra are then simulated using a potential step and current relaxation technique developed by Bessler (2007). For a more in-depth description of the methodology (including governing equations, boundary conditions and model parameters), the reader is requested to please refer to Banerjee and Deutschmann (2015).

Results

The model parametric study to examine the influence of cathode thickness and microstructure on the electrochemical performance is done at a temperature, T = 973 K and a partial pressure of oxygen of 0.21 atm with the porosity at the cathode current collector fixed at 0.4.

The results of the study are summarized in Figure 1. The polarization resistance (obtained from impedance simulations) decreases monotonically with a decrease in particle diameter which suggests that gas phase diffusion losses resulting due to increase in pore diameter is outweighed by the increase in LSM/YSZ interfacial specific surface area. This trend, however, is sensitive to the partial pressure of oxygen and under more reducing atmospheres, particle diameters under 0.1 µm may cause an increase in polarization resistance (Chen et al. (2004)). The influence of YSZ volume fraction also aligns with results presented by Chen who, for a particle size ratio of 1, found an optimal volume fraction of 0.55 as compared to the optimal value of 0.5 obtained in this study. The percolation thresholds of 0.35 to 0.65 are also typical for a particle size ratio of 1 and the figure makes clear that volume fractions beyond this range have a severe impact on cathode performance due to the loss of inter-connectivity of the phases.

Interestingly, the polarization resistance also attains a minima with varying cathode thickness. While it is clear from percolation theory that with increasing thickness, the increase in electrochemical reaction area is counterbalanced by the decrease in effective transport properties (due to increasingly poor phase connectivity), the relationship of thickness with polarization resistance is typically asymptotic (Virkar et al. (2000)). However, the present model has been fit to reproduce experimental results obtained by Barbucci et al. (2009) who had tested cathodes with a monotonic increase in porosity with thickness. This porosity gradient leads to the increase in resistance for thicknesses beyond 60 µm.

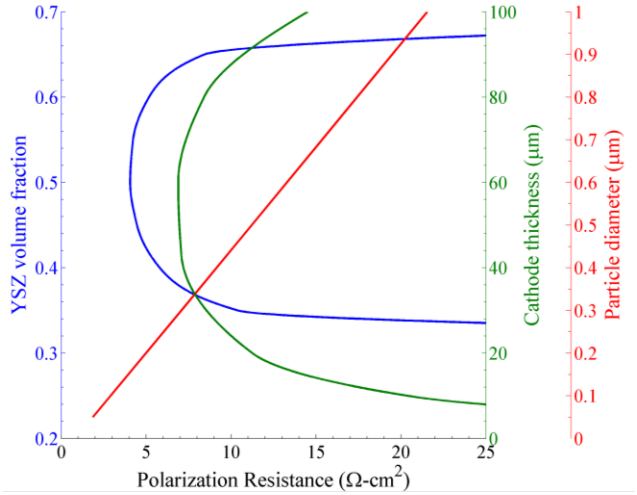

Figure 1. Effect of cathode thickness and microstructure on polarization resistance

Conclusions

Based on the numerical study, at an operating temperature of 973 K and a partial pressure of oxygen of 0.21 atm, the cathode polarization is minimum for a 60 µm thick LSM/YSZ composite cathode with particle diameter of 0.05 µm and equal volume fractions of LSM and YSZ.

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